Sulfonic acid-functionalized aerogels as high resistant to deactivation catalysts for the etherification of glycerol with isobutene

María Dolores González [a], Pilar Salagre [a], Elena Taboada [b], Jordi Llorca [b], Elies Molins [c], Yolanda Cesteros [a,*]

[a] Departament de Química Física i Inorgànica. Universitat Rovira i Virgili. C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain
[b] Institute of Energy Technologies and Centre for Research in Nanoengineering, Universitat Politècnica de Catalunya, Avda. Diagonal 647, ed. ETSEIB, 08028 Barcelona, Spain
[c] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

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ABSTRACT

Silica aerogel and lyogel have been successfully sulfonated in one step by a simple post-synthesis method using microwaves as well as conventional heating. The use of microwaves allowed loading higher amounts of sulfonic acid groups in both silicas, according to the higher S/Si atomic ratio determined by XPS, and the higher sulfur content determined by TGA, also exhibiting lower surface area and higher acidity. Sulfonated aerogels showed higher conversion and selectivity to h-GTBE (glycerol di- and tri-ethers) than sulfonated lyogels for the acid-catalyzed etherification of glycerol with isobutene. This was attributed to the higher content of sulfonic acid groups incorporated in aerogel. Microwave-assisted sulfonated aerogel yielded 75% of selectivity to h-GTBE, which can be used as fuel additive, for practically total conversion. Interestingly, larger porosity of aerogel avoided the partial blocking of pores by reaction products observed when other micro- and mesoporous catalysts were tested for this reaction. The combination of high conversion, high selectivity to h-GTBE, practically no formation of undesired di-isobutylenes and very high resistance to catalyst deactivation makes microwave-assisted sulfonic acid functionalized aerogel a promising catalyst for this etherification reaction.

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1. Introduction

Materials with high porosity and low density have attracted much attention because they combine the advantages of high surface area and high pore volume as well as larger pore size with the accessible diffusion pathways associated with nanoporous structures. Aerogels are unique low-density, open-cell porous materials that can be used as a robust material platform for designing novel nanoporous materials. Aerogels have a unique microstructure that consists of a branched skeleton of interlinked nanoparticles surrounding pores that are tens to hundreds of nanometers in size. Characteristic properties of silica aerogels are high porosity and large surface areas, which make this material very appropriate for catalytic purposes [1–6], besides low density, low thermal conductivity, high temperature stability and low dielectric constant. The unique characteristic features of silica aerogels arise from the fact that they are mainly composed of air. Silica aerogels are usually synthesized by sol–gel chemistry to form solvent filled gels, which are then dried under supercritical conditions [4,5]. When the silica alcogels are dried by lyophilization, silica lyogels are obtained [7]. Lyogels also have high surface areas but lower and narrower pore size distribution than aerogels [8]. There are few references about the use of lyogels, also called cryogels, in catalysis, and are mainly referred to the use of alumina and carbon lyogels as catalytic supports [9–12].

Sulfonic acid-functionalization of aerogels and lyogels can generate effective solid acid catalysts with enhanced catalytic properties due to the increase of the number and strength of Brønsted acid sites. There are two general approaches for functionalizing materials: post-synthesis grafting, in which the material is prepared and then functionalized, and co-condensation, where the functionalized silane is included in the material synthesis sol–gel mixture so that it is incorporated in the structure as the material forms [13]. There is just one recent study about the incorporation of sulfonic groups in aerogel in which 3-mercaptopropyltriethoxysilane was added during the synthesis of the aerogel prior to supercritical extraction. This procedure involved many consecutive long steps: mixing of reagents for 24 h, later ageing at 140 °C 24 h more, and after supercritical extraction, oxidation of the thiol groups with H_2O_2 to obtain the sulfonic

groups [14]. However, there are no references about the sulfonic acid-funcionalization of aerogels or lyogels by a simple post-synthesis method in one step.

The use of microwaves for the synthesis or modification of materials is becoming an important tool to decrease the synthesis time, with the subsequent energy saving, and to modify the sample properties, which can be of interest for catalysis [15–18]. There are no studies about the use of microwaves for the acid-functionalization of aerogels or lyogels.

Recently, special attention is focused in the obtaining of di- and tri-tertiary butyl ethers of glycerol, the so-called "higher ethers" (h-GTBE), by catalytic etherification of glycerol (glycerine, 1,2,3-propanetriol) with tert-butanol or isobutene in the presence of catalysts with Brønsted acidity [19–26]. h-GTBE is an excellent additive with a large potential for diesel and biodiesel reformulation. Thus, when h-GTBE was incorporated in standard 30–40% aromatic-containing diesel fuel, emissions of particulate matter, hydrocarbons, CO and unregulated aldehydes decreased considerably in the exhaust gases [27,28]. Moreover, h-GTBE can replace methyl tertiary butyl ether (MTBE), which is used as valuable additive because of its antidetonant and octane-improving properties, but is detrimental to the environment. Catalytic etherification of glycerol also constitutes a valuable green process since it allows the revalorization of glycerine, which is formed as by-product in significant amounts during biodiesel production (10 wt.% of the total product) [29–31]. In a previous work, we achieved high selectivity to h-GTBE with sulfonic acid-functionalized beta (88–91%) and sulfonic acid-functionalized SBA-15 (85–91%) catalysts for total conversion [26]. However, some deactivation occurred for both type of catalysts since a decrease of surface area was observed after reaction because of the presence of reagents and reaction products in the pores.

The aim of this work was to achieve the post-synthesis sulfonation of aerogels and lyogels by a simple one-step method using microwaves as well as conventional heating, in order to be tested as catalysts for the acid-catalyzed etherification of glycerol with isobutene. Samples were widely characterized by XRD, N_2 physisorption, TGA, XPS, FTIR and potentiometric titration techniques. Special attention was paid to study the catalytic life of the best catalyst.

2. Experimental

2.1. Preparation of the catalysts

Silica gels were synthesized by the sol–gel method [32] based on the hydrolysis and condensation of a silicon alkoxide, in our case tetramethoxysilane (TMOS). TMOS was first diluted in ethanol and stirred magnetically. Then, an aqueous solution of NH_3 0.65 M was added dropwise. The resulting solution, called sol, was stirred for 10 min, then poured into plastic tubes and closed to avoid solvent evaporation. After 40 min they gelified, giving rise to colourless and transparent alcogels. Additionally, some extra ethanol was added to the gels to avoid their drying. The TMOS/H_2O/EtOH molar ratio was 1/4/12.25.

The silica alcogels were dried following one of these two methods: lyophilization or supercritical drying [33]. Lyophilization required a pre-treatment of the alcogels: the ethanol inside the gel pores had to be exchanged by water. This was done by immersing the alcogels in water baths and changing the water at least 4 times during two days. The resulting hydrogels were then frozen in liquid nitrogen and connected to a lyophilizator, to reduce the pressure down to 0.05 mbar. The frozen water inside the silica pores was sublimated. The final material was a white and fluffy powder, denoted as lyogel (LG). On the other hand, the supercritical drying

consisted of placing the wet gels inside an autoclave and increasing the pressure and temperature over the supercritical point of ethanol (543 K, 200 bar). Then, the autoclave was depressurized, venting out the ethanol. The final materials, aerogels (AG), were transparent and very light monoliths.

Aerogel and lyogel were sulfonic acid-functionalized in one step by a simple method: 2 g of aerogel or lyogel were treated with 1.4 g of 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane (CSPTMS) solution in methylene chloride (50 wt.%, Gelest) in 2 M HCl solution at 313 K for 2 h using microwaves (Mile-stone Ethos-Touch Control equipped with a temperature controller) (samples SMw-AG and SMw-LG) or conventional heating (samples SC-AG and SC-LG). Two more sulfonated aerogel samples were prepared with microwaves by using lower (0.7 g) and higher (2.8 g) amounts of CSPTMS (samples SMw-AG(0.7) and SMw-LG(2.8)) All samples were filtered, washed extensively with deionised water and dried overnight.

Commercial Amberlyst-15, supplied by Aldrich (39 m²/g, pore size of 103 Å, acidity of 4.7 meq H⁺/g) was also tested for comparison.

2.2. Characterization methods

X-ray Diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using nickel-filtered Cu Kα radiation. Samples were dusted on double-sided sticky tape and mounted on glass microscope slides. The patterns were recorded over a range of 2θ angles from 10° to 90°.

Textural characterization of the solids was performed by N_2 ($\sigma_{N_2} = 0.162$ nm²) adsorption–desorption at 77 K using a Quadrasorb SI surface analyser. Before measurements all samples were outgassed at 423 K. The BET specific surface areas were calculated using adsorption data in the relative pressure range $0 < P/P_0 < 0.3$. Micropore and external surface areas were obtained by t-plot analysis of the adsorption data in the $3.5 \leq t \leq 5$ Å t range by adopting the de Boer reference isotherm equation, whereas pore volumes and pore size distributions were determined by the Barrett–Joyner–Halenda (BJH) method.

Thermogravimetric analyses (TGA) were performed with a TA instruments equipment from 50 °C to 800 °C at 10 °C/min under airflow.

XP spectra (XPS) were collected at a pressure below 5×10^{-7} Pa with a SPECS system using a Al anode XR50 X-ray source (150 W) and a 9-channel Phoibos 150 MCD detector with pass energy of 25 eV at 0.1 eV steps. Quantification of surface elements was carried out using Shirley baselines and Gaussian-Lorentzian (1:1) line shapes. Binding energy values were referred to the C1s adventitious signal.

Infrared spectra were recorded on a Fourier transform PerkinElmer Spectrum one spectrometer with a universal attenuated total reflectance (ATR) accessory.

Acid capacity was measured through the determination of cation-exchange capacities using aqueous sodium chloride (2 M) solutions as cationic-exchange agent. Released protons were then potentiometrically titrated [34].

2.3. Catalytic activity

Etherification experiments were performed in the liquid phase in a stainless steel stirred autoclave (150 mL) equipped with temperature controller and a pressure gauge. Stirring was fixed for all experiments at 1200 rpm to avoid external diffusion limitations. Liquid phase pressurized isobutene (glycerol/isobutene molar ratio of 0.25) was injected into the reactor, previously charged with glycerol and catalyst (0.5 g), using nitrogen at 10 bar as pushing agent. The temperature was then raised to 348 K and the pressure

increased accordingly following the liquid-vapour equilibrium. Catalytic experiments were performed for 24 h. The reaction products were analyzed by gas chromatography using a Shimadzu GC-2010 instrument equipped with a SupraWax-280 column and a FID detector.

Glycerol conversion and selectivity to MTBG (glycerol monoethers) were determined from calibration lines obtained from commercial products. For DTBG (glycerol diethers) and TTBG (glycerol triether), which were not available commercially, we isolated them from the products of the etherification reaction by column chromatography (1:9 ethyl acetate/hexane) and identified them by ^{13}C and ^{1}H NMR for proper quantification [26,35]. Turnover frequency values (TOF) were calculated as moles of glycerol converted per mole of active species (H^+) per hour.

3. Results and Discussion

3.1. Characterization of the catalysts

X-ray diffraction (XRD) patterns of the sulfonated samples showed the typical amorphous structure of silica aerogels and lyogels (Fig. 1), suggesting that sulfonation induces no crystalline changes in the samples.

N_2 adsorption–desorption isotherm of the initial non-sulfonated aerogel (AG) was mainly of type II (Fig. 2) corresponding to macroporous materials, as confirmed in the pore size distribution (Fig. 2) where some mesoporosity was also observed. N_2 adsorption–desorption isotherm of the initial non-sulfonated lyogel (LG) (Fig. 2) was of type IV associated to mesoporous materials, with pore sizes between 2 and 45 nm, as we can see in its pore size distribution (Fig. 2).

N_2 adsorption–desorption isotherm of the aerogel sulfonated by conventional heating (SC-AG) reminds that of the starting aerogel (mainly type II) (Fig. 3a) whereas the microwaved-sulfonated aerogel (SMw-AG) showed an isotherm mainly of type IV, attributed to mesoporous materials (Fig. 3b). For the latter sample there was a considerable decrease in the pore volume (0.62 vs. 4.77 cc/g, Table 1) and in the average pore size (35 vs. 65 nm) when compared to the non-sulfonated aerogel. This can be related to a higher incorporation of the sulfonic acid groups. On the other hand, N_2 adsorption–desorption isotherms of sulfonated lyogels (Fig. 3c and d) were very similar to that of the starting lyogel (type IV). However, the average pore size increased significantly for both sulfonated samples (from 10 to 30 nm), while the pore volume decreased from 1.60 cc/g (AG) to 1.47 cc/g (SC-AG) and 1.2 cc/g (SMw-AG) (Table 1). This suggests that the smallest mesopores, those below 10 nm in diameter, could be blocked by the sulfonic acid groups.
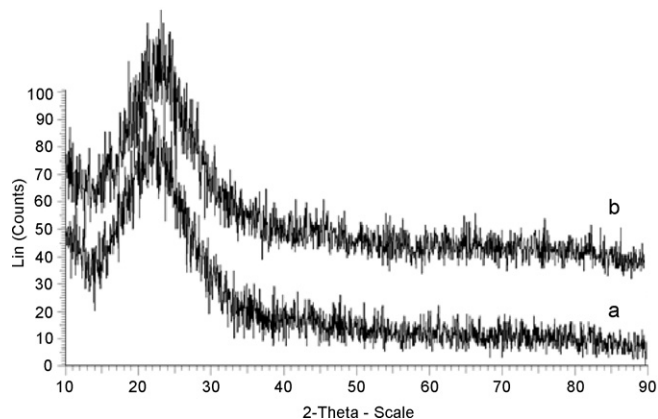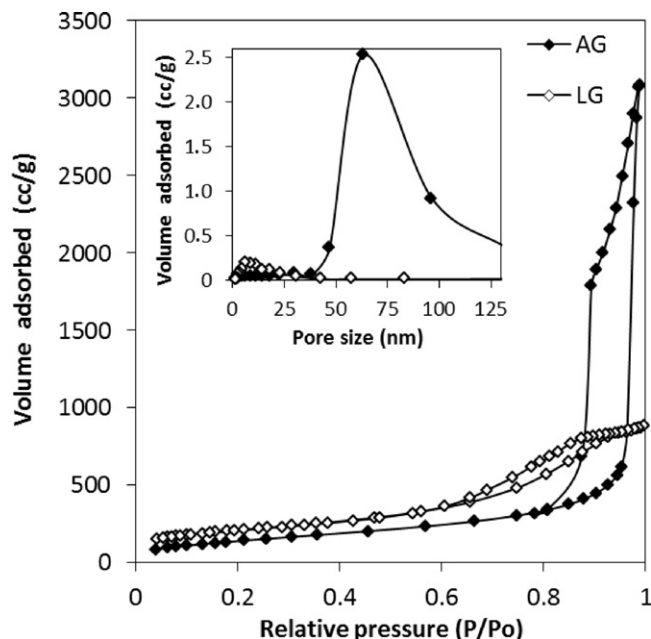

Fig. 2. N_2 adsorption–desorption isotherms and pore size distribution graphs of aerogel and lyogel.
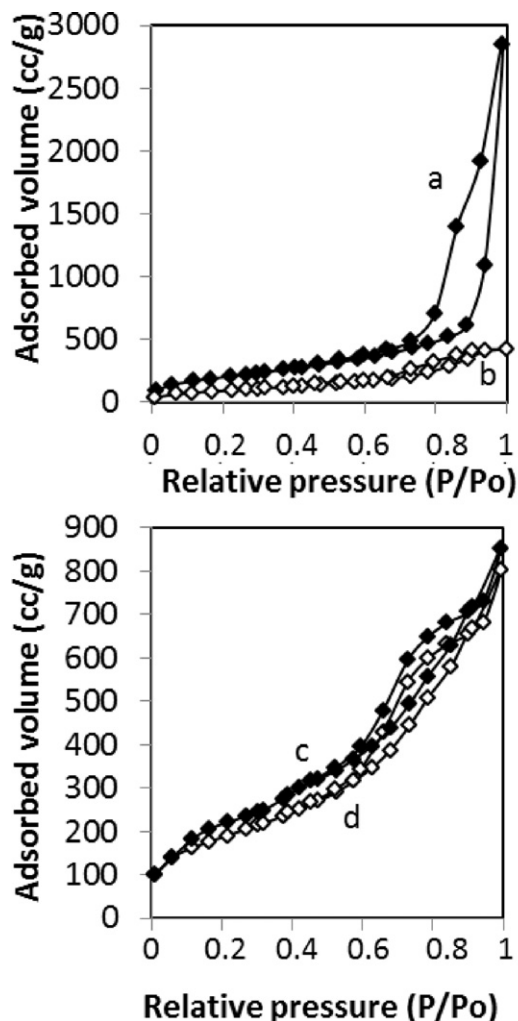

Fig. 3. N_2 adsorption–desorption isotherms of the samples (a) SC-AG, (b) SMw-AG, (c) SC-LG and (d) SMw-LG.

Fig. 1. X-ray diffractograms of samples a) SMw-AG and b) SMw-LG.

Table 1
Characterization of the samples.

| Samples	S/Si surface atomic ratio[a]	Sulfur content[b]	BET area (m^2/g)	Pore volume (cc/g)	Average pore size (nm)	Acid capacity[c]
AG	–	–	526	4.77	65	–
SC-AG	0.003	0.05	547	4.50	59	0.07
SMw-AG	0.031	0.22	353	0.62	35	0.24
SMw-AG(0.7)	–	0.04	537	3.20	48	0.05
SMw-AG(2.8)	–	0.27	211	0.48	22	0.30
LG	–	–	751	1.60	10	–
SC-LG	0.002	0.02	702	1.47	30	0.02
SMw-LG	0.006	0.04	669	1.2	30	0.04

[a] Determined by XPS.
[b] (mmol organic sulfonic acid group/g sample) calculated from TGA.
[c] Acid capacity obtained by potentiometric titration (meq H^+/g).

In order to confirm and quantify the introduction of the sulfonic acid groups, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) techniques were used. XPS is a useful technique for determining the type of sulfur species and measuring quantitatively the sulfonic acid groups at the surface [36,37] whereas the weight loss observed between 360 and 660 °C in the TGA of organosulfonated samples has been related in the literature to the loss of organosulfonic groups, [34,38] allowing us to calculate the mmol organic sulfonic acid groups/g sample (Table 1).

The S 2p XP spectra of the sulfonated aerogels and lyogels only showed one peak at ca. 168–169 eV associated with sulfate (S^{6+}) species due to sulfonic ($-SO_3H$) acid groups [33,34], with higher intensity for the microwaved samples (e.g. Fig. 4). The S/Si atomic ratios, calculated from XP spectra, were 0.003 and 0.031 for the sulfonated aerogels SC-AG and SMw-AG, respectively (Table 1). For sulfonated lyogels, the S/Si atomic ratios were 0.002 and 0.006 for SC-LG and SMw-LG, respectively (Table 1). Therefore, the use of microwaves for the sulfonic acid-funcionalization of aerogels or lyogels resulted in the introduction of higher amounts of sulfonic acid groups in the silicas than conventional heating, according to the higher S/Si atomic ratio determined by XPS, the higher sulfur content, determined by TGA [34], and the lower BET area and higher acidity observed for the samples sulfonated with microwaves (Table 1). The higher content of sulfonic acid groups introduced in the aerogel with respect to the lyogel sample using microwaves as well as conventional heating (Table 1) can be explained by the large pore size (meso-, macropores) of aerogel, and therefore, the higher accessibility of the silanol groups to the sulfonating agent (Scheme 1).

IR spectra of pure AG and LG samples are shown in Fig. 5. Lyogel is more hydrophilic than aerogel, as indicated by the more intense
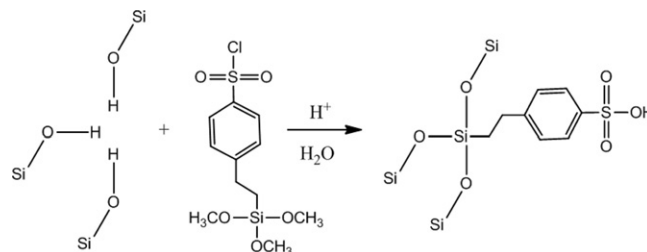
Scheme 1. Reaction of silanols with CSPTMS to form the organosulfonic groups.

bands of silanol groups (965 cm^{-1}, Si—OH), water (1637 cm^{-1}) and hydroxyl groups (around 3300 cm^{-1}). The higher content of silanol groups in the lyogel sample, together with its higher surface area (751 vs. 526 m^2/g) might forecast a better functionalization compared to the aerogel. However, the results are the opposite. We assume that the reason lies in the smaller pore size of lyogels, and therefore, a lower accessibility of the silanol groups to the sulfonating agent, which could block the smallest pores. Additionally, the more hydrophilic nature of lyogel, which can form stable colloids in aqueous solutions, could difficult the incorporation of the organosulfonic groups, resulting in less sulfonic acid-functionalization.

Sulfonation of aerogel with lower or higher amounts of sulfonating agent (CSPTMS) with microwaves (SMw-AG(0.7) and SMw-AG(2.8)) did not increase and slightly increased, respectively, the incorporation of sulfonic acid groups, as confirmed by the sulfur content and acidity capacity obtained for both samples when compared with SMw-AG (Table 1). For SMw-AG(0.7) the amount
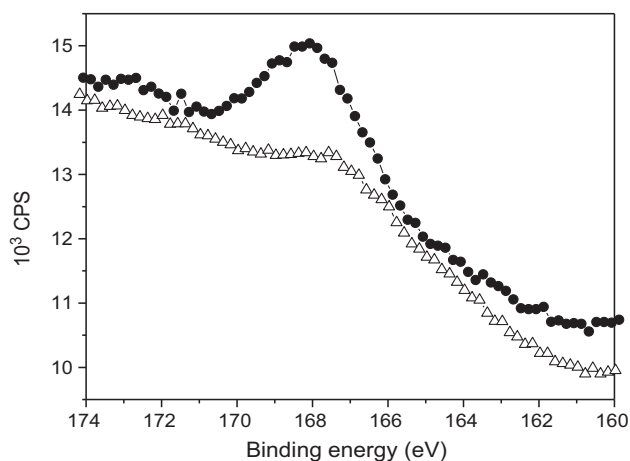
Fig. 4. XP spectra of samples SC-AG (empty triangles) and SMw-AG (full circles) in the S 2p core level region.
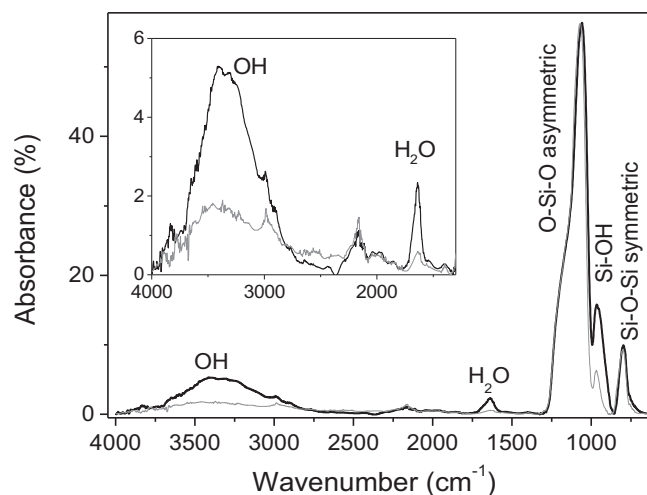
Fig. 5. FTIR of samples a) AG (grey line) and b) LG (black line). Inset shows zoom on 4000–1300 cm^{-1} region.

Table 2
Catalytic results for the glycerol etherification with isobutene after 24 h of reaction.

Catalysts	Conversion (%)	TOF[a] ×10 (h^{-1})	Selectivity to MTBG[b] (%)	Selectivity to h-GTBE[c] (%)
Amberlyst-15[d]	73	0.76	65	35 (3)
Amberlyst-15	99	0.17	23	77 (19)
AG	53	–	83	17 (0)
SC-AG[d]	71	32.10	82	18 (0.1)
SC-AG	96	7.24	56	44 (4)
SMw-AG[d]	79	8.93	72	28 (1)
SMw-AG	99	1.87	25	75 (17)
SMw-AG(0.7)	72	10.85	78	22 (0.1)
SMw-AG(2.8)	87	1.31	41	59 (7)
LG	0	–	–	–
SC-LG	37	8.37	100	0
SMw-LG	57	5.16	87	13 (0.3)

[a] TOF: Turnover frequency of glycerol conversion.
[b] MTBG: glycerol monoethers.
[c] h-GTBE: glycerol diethers + glycerol triether. In parenthesis, selectivity to glycerol triether (%).
[d] Reaction time: 4 h.

of CSPTMS was not enough to sulfonate all the available silanols whereas for SMw-AG(2.8) the excess of sulfonating agent partially blocked the pores. This explains the BET area values obtained for both samples (Table 1).

Taking into account that aerogels and lyogels are very sensitive to the evaporation of the liquid phase, often resulting in the collapse of the structure, the importance of this post-synthesis sulfonic-acid functionalization method is that we achieved to modify aerogels and lyogels in the liquid phase without destroying these structure of the materials, as confirmed by nitrogen physisorption.

3.2. Catalytic activity

Table 2 shows the catalytic activity results of aerogel and lyo-gel catalysts compared with that of a commercial Amberlyst-type catalyst for the etherification of glycerol with isobutene after 24 h of reaction. The main reaction products were mono-tert-butyl glycerol ether (MTBG), di-tert-butyl glycerol ether (DTBG) and tri-tert-butyl glycerol ether (TTBG). Additionally, di-isobutylene (DIB) was detected for commercial Amberlyst-15 (36.2 wt.%) and in very low amounts for sulfonated aerogel catalysts (<1 wt.%). Acid-based resins, such as Amberlyst, seem to be able to further dimerize the remaining isobutylene to produce the corresponding DIB, as previously reported by other authors [21,22].

Table 2 also depicts the catalytic results of some representative catalysts: Amberlyst-15, SMw-AG and SC-AG after 4 h of reaction. Initially these catalysts showed a similar behaviour: conversion values between 71 and 79%, and high selectivity to MTBG (65–82%). It is well known that the reaction of glycerol with isobutylene is a complex of three acid catalyzed consecutive equilibrium reactions [19–26]. This involves that first monoether is formed from glycerol and then, it is necessary that other isobutylene molecule reacts with the monoether to obtain the diether, and this needs to react with other isobutylene molecule to finally form the triether. The catalytic results observed after 4 h of reaction, confirm that initially, the activity of these catalysts is mainly related to the formation of the glycerol monoethers, leading to high TOFs, but longer reaction times were required to increase selectivity values to h-GTBE.

After 24 h of reaction, AG showed moderate conversion but low selectivity to h-GTBE whereas LG was not active for this reaction. These results can be explained by the presence of silanol groups with low acidity. The higher accessibility of the silanol groups of the aerogel with respect to lyogel, as commented above, can justify these catalytic results.

Sulfonic acid-functionalized aerogels and lyogels were more active, as expected, due to the presence of the sulfonic acid groups. Regarding the catalytic activity of sulfonated aerogels and sulfonated lyogels prepared with the same amount of sulfonating agent by conventional heating (SC-AG, SC-LG) or under microwaves (SMw-AG, SMw-LG), we observe that sulfonated aerogels showed much higher conversion, much higher selectivity to h-GTBE but lower TOF values than sulfonated lyogels (Table 2). It is also important to remark that glycerol triether was formed with sulfonated aerogels but only in very low or null amounts for sulfonated lyogels. The higher conversion and higher selectivity to the desired products obtained for sulfonated aerogels can be mainly attributed to the higher amount of Brønsted acid sites incorporated in these samples (Table 1). The higher TOF values of sulfonated lyogels for the glycerol conversion can be related to their higher surface area (Table 1) that should favour a better distribution of the acid centres and, therefore, the accessibility of the reagents to the acid sites, but can be also explained by the high selectivity of these catalysts towards glycerol monoethers (MTBG). Taking into account, as commented above, that etherification of glycerol with isobutylene consist of acid catalyzed consecutive equilibrium reactions, the formation of glycerol monoethers from glycerol is quite easy (see AG with low acidity, or the catalysts tested after 4 h of reaction, Table 2), leading to high TOFs but when the reaction evolves to the formation of diethers from monoethers or triether from diethers (e.g. SMw-AG after 24 h of reaction, Table 2), the value of TOF, which was calculated with respect to the glycerol converted, decreases, since at these conditions competing the three catalytic reactions, the formation of the monoether from glycerol should be less favoured. The lower amount of acid sites of sulfonated lyogels (Table 1) justifies their lower conversion and very low selectivity to h-GTBE. This confirms the importance of having appropriate Brønsted acidity (amount and strength) for this reaction.

For the aerogels sulfonated under microwaves with lower (SMw-AG(0.7)) or higher amounts (SMw-AG(2.8)) of sulfonating agent, lower conversion and lower selectivity to h-GTBE were obtained, as expected, due to the lower acid capacity of the sample sulfonated with lower amount of CSPTMS (Table 1), and the less accessibility of the acid sites for the sample sulfonated with higher amounts of sulfonating agent due to the partial blockage of pores because of the excess of CSPTMS used (Table 1). The higher TOF observed for SMw-AG(0.7) with respect to SMw-AG can be again related to the higher surface area of this sample (Table 1) which should favour a better accessibility of the acid sites, and to the higher selectivity towards MTBG obtained for this catalyst although its lower acid capacity led to lower conversion and selectivity to h-GTBE. In contrast, the lowest surface area of catalyst SMw-AG(2.8), due to the excess of sulfonating agent, explains its lowest TOF.

Interestingly, microwave-assisted sulfonated catalysts (SMw-AG, SMw-LG) showed higher conversion, remarkably higher selectivity to h-GTBE (and to the triether) although lower TOF values than those obtained for the catalysts sulfonated by conventional heating at the same conditions (SC-AG, SC-LG). The higher conversion and higher selectivity to h-GTBE can be again related to the higher amount of sulfonic acid groups introduced with microwaves whereas the higher TOF observed for the catalyst functionalized by conventional heating (SC-AG) is a consequence of its higher surface area (Table 1), which is also due to its lower functionalization, together with its higher selectivity towards MTBG (Table 2). In a previous work, we observed that the use of microwaves during sulfonic acid-functionalization of SBA-15 and zeolite Beta resulted in catalysts with higher conversion and selectivity to h-GTBE than those sulfonated by conventional heating [26]. The effect of microwaves on sulfonic acid-functionalization can be mainly related to the most homogeneous heating achieved with microwaves, which favours crystallinity of the synthesized samples [26,39].

Aerogel sulfonated with the optimum amount of CSPTMS under microwaves (SMw-AG) exhibited the best conversion (99%) and the best selectivity to the desired product, h-GTBE (75%) with 17% of selectivity to the triether. This catalytic result was comparable to that obtained with one commercial acid ion-exchange resin, Amberlyst-15, which is a typical acid catalyst used for this reaction (Table 2), but slightly lower with respect to the selectivity to h-GTBE than those obtained by testing sulfonic acid-functionalized beta (88–91%) and sulfonic acid-functionalized SBA-15 (85–91%) catalysts at the same reaction conditions [26]. This can be explained by the higher acidity capacity of these sulfonated Beta and SBA-15 materials associated with the incorporation of higher amounts of sulfonic acid groups [26]. All catalysts maintained the sulfur content after reaction, as determined by TGA. This confirms that there was not leaching of the sulfonic acid groups during reaction.

Interestingly, the best catalyst, SMw-AG, after 24 h of reaction, did not show appreciable changes in the N_2 adsorption–desorption isotherms and in the BET area value (Fig. 6). This means that the larger porosity of aerogel avoids the partial blocking of pores by the reaction products formed during the etherification reaction in contrast with other microporous (sulfonated acid-functionalized

beta) and mesoporous materials (sulfonated acid-functionalized SBA-15), which showed a considerable decrease of the surface area after reaction [26].

Catalytic life of catalyst SMw-AG was evaluated from four consecutive runs performed reusing the catalyst at the same reaction conditions used in the first catalytic test (Fig. 7). For comparison purposes, catalytic life was also studied for commercial Amberlyst-15 and for one microwave-assisted sulfonic acid functionalized SBA-15 (here called SBA-15-MwS), which was synthesized as previously reported [26] (Fig. 7). After each catalytic run, recovering of the catalyst was performed by filtration, mild-washing in ethanol and acetone at room temperature and dried before reaction. After the four consecutive catalytic runs, we observed a higher decrease of conversion for Amberlyst-15 than for SBA-15-MwS and SMw-AG catalysts, which showed just a slight conversion decrease (Fig. 7). This could be explained by the higher ability of Amberlyst-15 to dimerize isobutylene to di-isobutylenes, which can deactivate the catalyst, as previously reported [21,22]. When regarding the selectivity values, higher differences arose between the catalysts. Thus, according to the decrease of conversion, Amberlyst-15 had a significant loss of selectivity to h-GTBE leading to 88% of selectivity
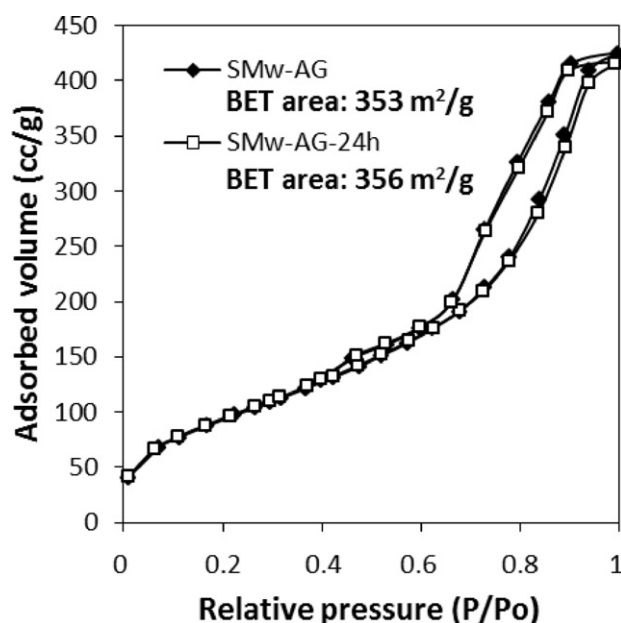
Fig. 7. Catalytic life of several catalysts for the etherification of glycerol with isobutene.

Fig. 6. N_2 adsorption–desorption isotherms of the catalyst SMw-AG before and after 24 h of reaction.

to MTBG and 12% of selectivity to DTBG after the 4 catalytic runs (Fig. 7). In the case of SBA-15-MwS, there is an initial loss of the selectivity to the triether, which evolved with the following catalytic runs to an increase in the formation of MTBG and a decrease of the selectivity to DTBG (Fig. 7). This can be related to the loss of surface area observed for this catalyst after reaction [26]. Finally, after the four runs performed reusing catalyst SMw-AG, just a slight loss of selectivity to h-GTBE accompanied by a slight increase of the selectivity to MTBG was observed (Fig. 7). This confirms that the larger porosity of aerogel avoids catalyst deactivation. The combination of high conversion, high selectivity to h-GTBE, practically no formation of undesired di-isobutylenes and very high resistance to catalyst deactivation makes microwave-assisted sulfonic acid functionalized aerogel an interesting catalyst for this etherification reaction, giving great added-value to the use of aerogels as catalysts.

4. Conclusions

Silica aerogel and lyogel were successfully sulfonic acid-functionalized in one step by a simple post-synthesis method using microwaves as well as conventional heating. The incorporation of the sulfonic acid groups was much higher in aerogel than in lyogel because of its larger pore size, which favoured the accessibility of the silanol groups to the sulfonating agent to incorporate the sulfonic acid groups. Samples sulfonated with microwaves showed higher incorporation of sulfonic acid groups than those sulfonated by conventional heating according to the higher S/Si atomic ratio, higher sulfur content, lower surface area and higher acidity observed.

Sulfonated aerogels showed higher conversion and higher selectivity to h-GTBE (glycerol di- and tri-ethers) than sulfonated lyogels for the acid-catalyzed etherification of glycerol with isobutene. This was related to the higher content of sulfonic acid groups, which led to higher amounts of Brønsted acidity. The best catalytic result was achieved with aerogel sulfonated with 1.4 g of sulfonating agent, which yielded almost total conversion and high selectivity to h-GTBE (75%). After four catalytic runs performed reusing catalyst SMw-AG, just a slight loss of selectivity to h-GTBE accompanied by a slight increase of the selectivity to MTBG was observed. The large meso-, macropores of aerogel avoided the partial blocking of the pores by the reaction products observed when other micro and mesoporous catalysts were tested for this reaction.

Acknowledgments

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